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2. Patent application number *(The Patent Office will fill in this part)* 0303230.7

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Technolox Ltd.
22 Ouseley Close
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Patents ADP number *(if you know it)* 8656533001

If the applicant is a corporate body, give the country/state of its incorporation UK

4. Title of the invention Method and apparatus for measuring the rate of permeation of gases and vapours through barriers and other materials

5. Name of your agent *(if you have one)*

"Address for service" in the United Kingdom to which all correspondence should be sent *(including the postcode)*

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11. I/We request the grant of a patent on the basis of this application.

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Method and apparatus for measuring the rate of permeation of gases and vapours through barriers and other materials

This invention relates to the measurement of the rate of permeation of a gas or vapour or a mixture of a gas and a vapour through a sample of a material (polymer, metal, ceramic material, composite, semiconductor, biological material or a combination thereof).

Background

Permeation is the process of species moving from one side of a medium through it and leaving it at the other side of the medium. Measuring the rate of permeation (or the rate of transmission) of vapours and gases through materials, in particular barrier materials, is important in various fields. Examples are packaging of food, of medical supplies and of electronic components. Other examples are fuel cells and fuel tanks. Barrier layer is used in this context as a layer with the purpose to prevent or restrict the passing of a gas or vapour through a material. The widely used instruments of MOCON Inc. Oxtran and Permatran (trade marks) use electrochemical and infrared sensors for the detection of oxygen and water vapour, respectively (see for instance US Patent 5390539). Mass-spectrometric methods are known to be used as detectors for measuring the rate of permeation (see for instance US Patent application 2003/0001086A1).

In some known application a gas cell is filled outside the vacuum chamber with an amount of liquid and then introduced into a vacuum chamber. After some time an atmosphere is established inside a gas cell, which contains vapour of the said liquid at a partial pressure relating to the vapour pressure of the liquid. In the case of water and water vapour a relative humidity of 100% is established inside the gas cell. Other methods use a carrier gas to sweep the permeated species to a detector. These methods create a number of difficulties and limitations.

- The vapour pressure of a vapour or gas above its liquid phase is unequivocally linked to its temperature by physical law. This means, if the vapour pressure is generated above a liquid phase, the pressure inside the gas cell cannot be varied at a fixed temperature. In the case of water vapour generated above liquid water this means, that the relative humidity inside the gas cell cannot be varied, it is always 100%. In some applications fixing the temperature and testing samples at different vapour pressures or in the case of water vapour at different relative humidity may be required.
- The unequivocal link between temperature and vapour pressure further means, that at different temperatures the said pressure is different. In testing samples, it might be an advantage to test samples at a constant pressure at different temperatures. For instance, testing procedures for displays in the automobile industry require testing above 80°C.
- Filling the gas cell under ambient conditions with an amount of liquid water means that the remaining volume is filled with atmosphere, usually at a pressure of around 1000 mbar. Inside the vacuum chamber the pressure is very low, which means there is a pressure differential of about 1000 mbar between both sides of the sample. This pressure differential causes stress to the sample, which may alter its permeation characteristics or cause damage to the test sample.
- Testing at the vapour pressure of the gas or vapour above its liquid phase (in the case of water vapour at a humidity of 100%) gives the maximum pressure difference between the inside of the gas cell and the vacuum in the vacuum chamber. The disadvantage of putting stress on the sample becomes more important at elevated temperatures. The vapour pressure of a saturated atmosphere of water vapour at 100°C is around 1000 mbar. Because of this relatively high pressure it is desirable to test samples at these temperatures at lower pressures.
- Furthermore, the gas species from the atmosphere trapped inside the gas cell will permeate through the sample too. It is not sufficiently known, to what extent the presence of such "impurities" influence the permeation of the sample vapour or gas.
- Mounting the sample in a gas cell limits the sample to simple shapes such as sheet material. More complicated structures, including complete electronic devices such as batteries, or sub-assemblies of devices are difficult to test in this arrangement. In particular, the measurement of permeation through edges (circumference) of the test sample is difficult, if not impossible.
- Most conventional methods are unsuitable for investigating the permeation of dangerous gases or vapours such as radon (radon permeates through building structures) because they need a great amount of the permeating gas or vapour
- All conventional methods measure the average rate of permeation of the sample, i.e. they do not provide information about whether the permeation through the sample (barrier layers and other samples) is homogeneous or varies across the sample due to defects or other inhomogeneities.

- Most conventional methods measure the sample temperature by means of a thermocouple. This method suffers from a lack of accuracy because in the case of a film sample it is difficult to attach the thermocouple directly to the film without damaging it.

Essential technical features

According to the present invention a method and an apparatus of measurement of the rate of permeation to alleviate the problems described above is presented.

Filling gas container with gas or vapour

In the **first** aspect of the invention a method and an apparatus are provided to measure the rate of permeation of a gas or vapour or mixture thereof through a test sample, which may be a barrier layer comprising:

- Filling the gas container covered with the test sample with an amount of gas or vapour inside a special filling vacuum chamber
- Transferring the gas container with the test sample to a vacuum chamber with vacuum and arranging the gas container in a way that the test sample faces a mass spectrometer to measure the partial pressure of the vapour species after permeation through the barrier layer
- using a specially formed gas container to limit the effect of decrease of partial pressure
- using a volume compensating device to keep the pressure inside the gas container at a constant value.
- Concluding the rate of permeation from the measured partial pressure
- Using a calibration procedure to estimate the rate of permeation

The first aspect of the invention has the advantage that the gas container can be filled with a gas or a vapour or a mixture thereof to any given pressure up to its vapour pressure (measured above its liquid phase). Another advantage is the exclusion of ambient gas from the interior of the gas container. A further advantage of filling the gas container with a gas or vapour at a low pressure is, that it reduces the pressure difference during the experiment and hence the stress acting on the test sample. Yet another advantage is the possibility of conditioning the test sample under the clean environment of a vacuum prior to filling with a gas or a vapour (for example outgassing or annealing of the test sample).
The rate of permeation of the test sample is estimated including a calibration procedure, where a range of samples with known rate of permeation is measured and the rate of permeation of the unknown test sample is then extrapolated from these values by using the measured partial pressure of the gas or vapour after permeation through the test sample. A calibrated gas leak can be used for calibration purposes too. The advantage of using a calibration procedure is that it gives an absolute value of the rate of permeation. The advantage of using a calibration procedure involving a number of samples with a known rate of permeation is its increased accuracy.
The advantage of using compact gas containers in an ultra-high vacuum chamber is, that test samples can be investigated at hazardous conditions (very low or high temperatures, radioactive or poisonous gases or vapours).

Filling the gas container with water vapour

In the **second** aspect of the invention (application of the first aspect to a specific permeating substance) a method and an apparatus are provided to measure the rate of permeation of water vapour through a test sample, which might be a barrier layer, comprising:

- Filling the gas container covered with the test sample inside a special filling vacuum chamber with an amount of water vapour at the desired relative humidity
- Transferring the gas container with the test sample to a vacuum chamber with vacuum and arranging the gas container in a way that the test sample faces a mass spectrometer to measure the partial pressure of the water vapour after permeation through the test sample
- Concluding the rate of permeation from the measured partial pressure
- Increasing the sensitivity of the experiment by including water isotopes $D_2{}^{16}O$, $D_2{}^{17}O$, $D_2{}^{18}O$, $H_2{}^{16}O$, $H_2{}^{17}O$, $H_2{}^{18}O$ as the background pressure inside the UHV-chamber varies between different mass/charge values and using isotopes with mass/charge ratios corresponding to low background values
- Alternatively (to using a mass spectrometer as detector), permeation of pure gases and vapours through suitable test samples can be estimated by using a pressure gauge of sufficient sensitivity to detect changes of the total pressure

The advantage of the second aspect is the possibility to test samples according to procedures that require a relative humidity of less than 100%. The relative humidity inside the gas container can be adjusted by

conventional methods such as using saturated or unsaturated solutions, in particular salt solutions. The advantage of this method is its simplicity. The relative humidity can also be adjusted by other means such as using specially engineered gas containers. The advantage of such gas containers is, that the relative humidity can be adjusted steadily to any desired value. Gas container with a variable inner volume have the advantage of offering the possibility to change the relative humidity during the measurement without disruption. Yet another advantage is the exclusion from ambient gas from the interior of the gas container, which, for instance makes it easier to exclude the influence of oxygen on the water vapour permeation. The advantage of using water vapour isotopes with a low background pressure is an improved signal to noise ratio. The advantage of filling the gas container with water vapour at a low pressure is, that it reduces the pressure difference during the experiment and hence the stress acting on the test sample and the undesirable bulging out of the test sample. Yet another advantage is the possibility of conditioning the test sample under the clean environment of a vacuum prior to filling with water vapour (for example outgassing or annealing of the test sample).

Permeation through samples other than films

The preceding paragraphs explained a method to study gas and water permeation through test samples, which are preferably flat. In many areas, such as microelectronic packaging and displays (such as displays based on OLED technology, where permeation through the edges is of interest too), the preparation of the geometric area of interest may not be possible in the form of a film or a similar simple shape. Examples are fuel cells, fuel tanks, batteries, transistors etc.

In the **third** aspect of the invention a method and an apparatus are provided to measure the rate of permeation of gases and vapours through complete devices or sub-assemblies thereof comprising:

- A means for filling the device or sub-assembly with the gas or vapour of interest
- A means of transferring and positioning the test sample (as described in the 1st and 2nd aspects)
- A sample holder to manipulate the test sample in the vacuum chamber, either manually or automatically.

The advantage of the third aspect of the invention is that cumbersome preparations of proxy test samples, which are made to fit the measurement kit, is not necessary. Test samples can be tested in the shape of their final application. This advantage opens up a new field for permeation measurements because not all samples can -even with shortcomings- be prepared in a suitable shape for conventional permeation measurement.

Position resolved permeation measurement

In the **fourth** aspect of the invention a method and an apparatus are provided to measure the rate of permeation of gases and vapours through samples at different locations on the test sample comprising:

- A device to collect and guide (to the mass spectrometer) gas or vapour molecules coming only from the region of interest on the test sample
- A means to move the gas container with the test sample and the mass spectrometer with respect to each other to expose different regions on the test sample to the mass spectrometer
- An encapsulation of the mass spectrometer, which can be, pumped separately having an entrance hole of approximately the area on the test sample to be investigated, which is corresponds to a diameter of around 1 mm or less

The advantage of this aspect is, that it opens up the possibility to study whether the rate of permeation depends on the location of the test sample. When studying complete devices or sub-assemblies (see third aspect of invention) the test sample may contain different parts where the permeation is different. Conventional methods only measure the average rate of permeation. It is an advantage to be able to distinguish the contributions to the rate of permeation originating from different areas of the test sample. Another advantage is, that a number of test samples can be mounted on a gas container with reservoirs containing different gases or vapours or gases or vapours under different conditions (for example at different pressures) such significantly increasing throughput of test samples.

Yet another advantage of such a method being available is, that test samples which use locally varying rates of permeation to achieve other effects such as drug release, can be investigated.

Infrared temperature measurement

In the **fifth** aspect of the invention a method and an apparatus are provided to measure temperature of the test sample during the permeation experiment by detecting radiation emitted from the test sample by means of a detector such as a pyrometer. Such a method does not require a sensor in physical touch with the test sample. The advantage of measuring the temperature of the test sample with a pyrometer or similar device is, that it gives temperature information directly from the test sample. Another advantage is the quick response of such a temperature sensor, that temperature changes can be detected almost

immediately. Yet another advantage is the possibility to focus the measurement signal to a spot size of a few mm or less, which permits taking temperatures at different locations of the test, samples.

Examples for implementation

A method as specific embodiment of the invention will now be described by way of non-limiting example with reference to the accompanying drawings in which:

Figure 1 shows a perspective view of the apparatus used in the method

Figure 2 shows a diagrammatic view of the filling chamber used in this method
a) gas container opened, gas or vapour may enter the gas container
b) gas container closed, filling chamber can be evacuated

Figure 3 shows gas containers used in the first aspect of the method
a) perspective view of a gas container containing four reservoirs
b) top view of a gas container containing four gas/vapour reservoirs
c) cross section of a gas container containing four gas/vapour reservoirs
d) first alternative shape of a gas container, perspective view of a gas container with increased volume to sample area ratio
e) first alternative shape of a gas container, cross section of a gas container with increased volume to sample area ratio containing a coil
f) second alternative shape of a gas container, cross section of a gas container with increased volume to sample area ratio
g) third alternative shape of a gas container, perspective view of an enclosing gas container
h) third alternative shape of a gas container, cross section of an enclosing gas container with a plug
i) fourth alternative shape of a gas container, cross section of an enclosing gas container consisting of an lower and an upper part
j) fifth alternative shape of a gas container, perspective view of an enclosing gas container coated with an impermeable layer
k) sixth alternative shape of a gas container, cross section of an enclosing gas container, with an area of reduced thickness
l) seventh alternative shape of a gas container, cylindrically shaped
m) eighth alternative shape of a gas container, showing a cross section with test sample and lid
n) eights alternative shape of a gas container, top view, showing lid with supporting mesh
o) ninth alternative shape of a gas container, showing a cross section with test sample and lid
p) ninth alternative shape of a gas container, top view, showing lid with supporting hole structure
q) tenths alternative shape of a gas container for position resolved measurement
r) eleventh alternative shape of a gas container with bellow
s) twelfth alternative shape of a gas container with piezoelectric components
t) thirteenth alternative shape of a gas container, perspective view of a container for position resolved measurements
u) thirteenth alternative shape of a gas container, top view of lid for container for position resolved measurements
v) thirteenth alternative shape of a gas container, cross section of a container for position resolved measurements
w) thirteenth alternative shape of a gas container, top view of alternative lid for container for position resolved measurements comprising a mesh
x) thirteenth alternative shape of a gas container, cross section of alternative lid for container for position resolved measurements comprising a hole structure
y) fourteenth alternative shape for a gas container where the test sample is located between gaskets

Figure 4 shows multi-stage gas containers
a) two containers with one valve located between the upper part and the lower part
b) first alternative shape with two valves between upper and lower part
c) a three-stage gas container comprising three units, separated by valves

Figure 5 shows different shapes of test sample assemblies
a) perspective view of a box-like assembly
b) cross section of a box-like assembly with areas of different rates of permeation for small edge-like test samples
c) first alternative shape of an assembly for flat film-like test samples , cross section
d) second alternative shape of an assembly with an enclosure, cross section
e) third alternative shape of an assembly with an enclosure, cross section

f) fourth alternative shape of an assembly showing a disk-like test sample with areas of different rates of permeation
g) fifth alternative shape of a hemispherical assembly in perspective view
h) fifth alternative shape of an assembly showing a hemispherical test sample in cross section

Figure 6 shows a diagrammatic view of structural details of an enclosure of a mass spectrometer and possible arrangements of the gas container relative to the mass spectrometer detector, and methods for cooling the enclosure of the mass spectrometer
a) mass spectrometer with a cylindrical enclosure, the enclosure having a small hole
b) first alternative shape of a cylindrical enclosure housing a mass spectrometer, the end of the enclosure having a small tube
c) second alternative shape of a cylindrical enclosure (housing a mass spectrometer) with a conical end, the conical end having a small hole
d) third alternative shape of a cylindrical enclosure (housing a mass spectrometer) with a conical end, the conical end having a small hole with a small tube
e) possible path of travel of gas molecules between a test sample and the enclosure of the mass spectrometer, flat bottom of enclosure without tube
f) possible path of travel of gas molecules between a test sample and the enclosure of the mass spectrometer, flat bottom of enclosure with tube
g) possible path of travel of gas molecules between a test sample and the enclosure of the mass spectrometer, conical bottom of enclosure
h) fourth alternative shape of a mass spectrometer with a cylindrical enclosure with a conical end, the conical end having a small hole and a small tube in contact with a gas container
i) fifth alternative shape of a mass spectrometer with a cylindrical enclosure with a conical end, the conical end having a small hole and a small tube in contact with a gas container
j) mass spectrometer with a cooling facility
k) first alternative shape of mass spectrometer with a cooling facility
l) circular shaped test sample with areas of different rates of permeation
m) rectangular test sample with stripe-like areas
n) gas container as gas or vapour source providing permeation of a gas or vapour or mixture thereof to a small area

Figure 7 shows a diagrammatic view of the arrangement of the mass spectrometer, the gas container and the detector with respect to the vacuum chamber
a) with a gas container having a transparent bottom
b) with a gas container made entirely of transparent material

Concerning the **first aspect** of the invention an experiment may be carried out as follows:
The purpose of the experiment is the measurement of the rate of permeation of a gas or a vapour through a test sample.

Preparation
Figure 1 shows an example for a vacuum system mounted onto a frame 19, which can be used for the method described herein. A gas container (see also figure 3) is introduced through the door 1 into the filling chamber 15. During this operation the valve 5 is closed to keep the investigation chamber 2 under vacuum. After introduction of the gas container the door 1 is closed and the filling chamber 15 is evacuated by means of a turbomolecular pump 6 with the gate valve 16 open.
After reaching a sufficiently low vacuum in the filling chamber 15, the gate valve 16 is closed and the gas or vapour of interest is admitted to the filling chamber 15. This can be done by conventional means such as attaching a pressurised gas bottle 17 containing the gas or vapour of interest to the filling chamber 15. The gas bottle 17 is separated from the filling chamber 15 by a valve 18 as shown in figures 2a and b. Once the valve 18 is opened, the filling chamber fills up with the gas or vapour to a certain pressure, which may be monitored by a pressure sensor 4 and which may be regulated by a valve 18. The gas or vapour enters the gas container through one or more filling holes 29 provided as shown in fig. 2a and b; see also fig. 3).

Filling
Figure 2 shows details related to the filling procedure of the gas container with a gas or vapour.

After a sufficient period of time the interior of the gas container is at the same pressure as the interior of the filling chamber 15. Now the valve 105 is closed. The operation of the valve 105 can be done by means of a suitable tool. Figures 2a and b illustrate the operation of a valve of the gas container. Figure 2a shows the "open" position and figure 2b shows the "closed" position. The gas container 23 covered with a test sample 21, which is mounted with a lid 22, is located inside the filling chamber 15. The valve 105, which contains a thread and can be screwed in and out, is in the "open" position (fig. 2a). After sufficient gas or vapour is inside the gas container 23 is closed by means of a suitable tool 26 (fig. 2b). The tool 26 shown in figures 2a and b has a blade similar to a screwdriver, but it may have other shapes such as a socket. It is operated by rotating a handle 25, which is connected to the tool 26 by means of a rotary feedthrough 27 (fig. 2b). For a more flexible handling a flexible hose or a bellow 24 can be attached to the feedthrough 27. If necessary, the gas container 23 can be moved inside the filling chamber by a manipulating device 28.

Gas container

Figure 3 shows a number of gas containers.

The gas container must be sufficiently small to fit through the door 1 of the filling chamber 15 and through the gate valve 5, which separates the filling chamber 15 and the investigation chamber 2. Figures 3a, b and c illustrate a possible shape of such a gas container. The body 101, which is preferably made of a material with a low rate of permeation such as a metal, contains one or more permeation holes 102 opening to the top. These holes are covered with the test sample(s). The test samples may be mounted to the body of the gas container by a lid 103. Mounting can be done by various techniques such as clamping, fixing with screws and gluing. The body 101 has a further set of filling holes 104, each fitted with a closing device such as a valve 105. The number of permeation holes 102 corresponds to the number of filling holes 104. The purpose of the valve 105 is to separate the holes 102 from the vacuum of the filling chamber 15 and from the vacuum of the measurement chamber 2, when the holes 102 are covered with a test sample.

Transfer

The filling chamber is evacuated once more by starting the turbomolecular pump 6 and opening the gate valve 16. After some time the pressure inside the filling chamber 15 will be sufficiently low for the gas container to be transferred into the investigation chamber 2. The transfer from the filling chamber into the investigation chamber is done by opening the gate valve 5 and moving the gas container by means of the transfer arm 3 into the investigation chamber 2. The gas container will be put on a sample holder 7 and the transfer arm withdrawn to its original position and the gate valve closed. The gas container will be positioned close to the mass spectrometer 12 by means of three screws 8, 9, 10. For increased accuracy these screws could be micrometer screws.

Measurement of the rate of permeation and calibration

After positioning the sample the partial pressure of the gases or vapours of interest will be monitored by means of the mass spectrometer 12 and the output signal of the mass spectrometer will be recorded on a conventional personal computer. The partial pressure measured by the mass spectrometer can be used to derive the rates of permeation. This can be done for individual species or for groups of several species of the gas or vapour.

The method of deriving permeation rates will be described in greater detail now. Under suitable experimental conditions the partial pressure detected by the mass spectrometer will assume a constant value after some time. This value of the partial pressure is a measure for the rate of permeation of the test sample. In order to quantify the rate of permeation a calibration process is carried out.

A range of samples is selected and the rate of permeation through these samples is established by conventional methods such as MOCON Permatran, Oxtran, the time-lag method or another conventional method. The same samples are investigated with the mass spectrometric method described herein according to the procedure described in the first and second aspect of the invention. A diagram is drawn (preferred in double logarithmic representation) showing the rate of permeation as measured by the conventional method on the x-axis and the partial pressure on the y-axis. The unknown sample is then investigated, the partial pressure estimated and the rate of permeation is taken from the diagram by extrapolation. Likewise, regression algorithms can be used, which can be implemented on a computer.

An alternative experiment is to use a pressure sensor measuring the total pressure of all samples and relate the total pressure measured by this sensor to the partial pressure measured by the mass spectrometer. As the rate of permeation of the calibration samples is known (i.e. from the literature), the rate of permeation for the test sample can be derived from its total pressure with an extrapolation procedure similar to that described above.

Preventing depletion

An essential feature of the method is that the gas or vapour inside the gas container cannot be replenished during the experiment. Nevertheless, reducing depletion of the gas or the vapour inside the gas container is desirable because the rate of permeation can be estimated more accurately from a constant level of partial pressure reading of the mass spectrometer as function of time.

Limiting depletion can be achieved by choosing a suitable shape of the gas container. Among the geometric parameters of the gas container the area of the opening has the biggest influence on the rate of permeation. The rate of decrease of the pressure inside the gas container depends on the amount of gas or vapour that leaves the gas container due to permeation with respect to the total interior volume of the gas container. In other words, a high ratio between the internal volume and the area of the opening is desirable in order to keep the permeation at a steady value. Figures 3d and e show the first alternative shape of the gas container consisting of a body 107 and a lid 108 containing an opening 109. In order to minimize depletion of the gas or vapour in the gas container, a high ratio between the internal volume of the gas container 112 and the exposed surface area 110 of the test sample 113 is required. This can be achieved by the shape shown in cross section in fig. 3e, where the gas container 107 extends into a much greater volume as the projection of the exposed area 110 of the test sample 113. Figure 3f shows the second alternative shape, where a high volume to surface area is achieved by having a coiled tube 114 inside the gas container 107.

The following calculations provide an illustration of the possible effect of the shape of the gas container on the rate of depletion of gas or vapour inside the gas container:

Assuming a flat test sample of 100μm polypropylene with an oxygen permeation of about $800cm^3/m^2/day$ at 25°C and a pressure difference of 1000mbar. Further assuming a diameter of d=3mm the exposed are of the test sample would be $\pi/4*d^2=7.1mm^2$. This gives a permeation of $5.7mm^3$ of oxygen per day for this test sample under the given conditions. A gas container as shown in figure 3a-c with a depth of 5 mm has an inner volume of $7.1mm^2*5mm=35.5mm^3$. This means that at a pressure difference of 1000 mbar 16% ($7.1mm^3/35.5mm^3$) of the gas permeates through the test sample within a day. A constant signal of the oxygen partial pressure cannot be expected under these circumstances.

Using a gas container similar to the shape shown in figure 3e the same exposed area of the test sample ($7.1\ mm^2$) is assumed. If the internal volume of the gas container 112 is greater than $100*5.7mm^3=570mm^3$, which is the amount of oxygen permeating through the test sample in one day, the loss of oxygen will be less than 1% per day and a constant signal of the partial pressure –within experimental error- can be expected during the usual duration of the experiment which is about one day. A diameter of 9mm and a height of 9mm of the internal volume 112 of the gas container shown in figure 3e fulfil this requirement.

Alternative shapes of the gas container

Figure 3 shows alternative shapes of gas containers.

Figure 3 g shows the third alternative shape of the gas container in perspective view. The gas container is made of the sample material 120, which eliminates the need for fixing the test sample to the container. Figure 3h shows a cross section of such a gas container 120, where the filling takes place through a hole in the bottom, which can be closed by a plug 121.

Figure 3i shows the fourth alternative shape without plug, where the gas container is made from an upper part 121 and a lower part 122, which are joined after filling. The joining may be done by welding in the case of polymers and metals and gluing in cases where welding is not appropriate. In order to restrict permeation into the investigation chamber 2, figure 3j shows in the fifth alternative shape how the gas container 120 can be covered with an impermeable layer or a layer of much lower rate of permeation 123 such as a metal leaving an uncovered opening 124 for the gas or vapour permeation.

Figure 3k shows the sixth alternative shape to achieve a reduced permeation through the container, where the gas container 120 has a reduced thickness at the region 125 facing the mass spectrometer.

Figure 3l shows the seventh alternative shape of the gas container where the body of the gas container 129 and a fitting lid are of cylindrical shape.

Figures 3m and n show the eights alternative shape of the gas container. The test sample 131 is mounted between the body 130 and the lid 132. For mechanical support and for better thermal connection of the test sample the lid contains a mesh133.

Figures 3o and p show the ninth alternative shape of the gas container. The test sample 135 is mounted between the body 134 and the lid 136. For mechanical support and for better thermal connection of the test sample the lid contains a plate with a number of holes 137.

Figure 3q shows the tenth alternative shape of the gas container. Similar to the shape shown in figure 3o and p the lid 136 is now of homogeneous thickness and the holes 138 extend to the surface of the lid.

Figure 3r shows the eleventh alternative shape of the gas container. The body of the gas container 140 has a hole 142 in the bottom, where a movable part 141 such as a flexible hose or an edge welded bellow is

joined to the body 140. By moving the movable part 141 up or down, the volume 144 inside the gas container 140 can be changed, which leads to a change of pressure of the gas or vapour inside the gas container. For an ideal gas at a constant temperature the product of volume and pressure is a constant p*V=const..
Figure 3r shows the twelfth alternative shape of the gas container. The body of the gas container 145 is made of a piezoelectric material. By applying a dc-voltage 146 to the body 145 the body can expand or shrink such changing the internal volume 147 of the gas container 145, which, leads to a change of pressure of the gas or vapour inside the gas container. Capacitive sensors 148 inside the gas container can be used as pressure sensors. The shapes as shown in figure 1.3r and s can be used to compensate for the loss of gas or vapour due to permeation through the test sample. The shapes as shown in figure 1.3r and s can also be used for changing conditions during the experiment without disruption.
Figures 3t-x show the thirteenth alternative shape of the gas container where the exposed sample region is long and very thin. The test sample 151 is mounted between the body of the gas container 150 and the lid 153. The small opening 154 of lid and body makes it suitable for the investigation of thin and long samples. Figure 1.3 w shows an alternative shape for the lid 153, which has a mesh 155 for sample support and improved thermal contact. Figure 1.3 x shows an alternative shape for the lid 153, which contains holes 156. Such a lid is particularly useful for position resolved permeation measurements.
Figure 3y shows a test sample 157, which is contained between two gaskets 158.

Two-stage filling chamber

If filling the gas container with gas or vapour at a particular desired vapour or gas pressure is not possible for some reason, but filling at another higher than the desired pressure is possible, a special shape of the gas container may be used. Figure 4a shows such a two-stage assembly comprising a lower part (the reservoir with the volume V_1) 160 and an upper part (the gas container with the volume V_2) 161 and the test sample 166. In the first place, both parts 160 and 161 are evacuated are evacuated with the valves 162 and 163 open. Then valve 163 is closed and the lower part 160 is filled with the gas or vapour of interest. After the lower part is filled, valve 162 is closed. If valve 163 is now opened, gas or vapour will enter both lower part 160 and upper part 161. Because the same number of molecules is now occupying the volume V_1+V_2 instead of volume V_1, the pressure of the gas or vapour is reduced. In the absence of sinks, the resulting pressure will be $p=V_1*p_{fill}/(V_1+V_2)$ with p_{fill} the pressure the lower part 160 was initially filled with. The upper part 161 and the lower part 160 may be detachable.
Figure 4b shows the first alternative shape where the valves 164 and 165 replace the valves 162 and 163, respectively, which are located between the upper part and the lower part. Opening and closing of the valves can be done by means of a closing device, similar to the illustration in figure 2.
Another alternative shape of a gas container is discussed below (figure 4c) with respect to the second aspect of the invention, which can also be applied for suitable vapours in the context of the first aspect.

Concerning the **second aspect** of the invention an experiment may be carried out as follows:
The purpose of the experiment is to measure the rate of water vapour permeation through a test sample. The sample transfer proceeds in the same or a similar way as described in the first aspect of the invention. The gas containers discussed in the first aspect can in principle be used for the experiments with water vapour. To achieve different degrees of humidity a number of methods can be used. It is well known, that certain saturated salt solutions have a water vapour pressure that is less than the vapour pressure established above pure water. Examples are given for the relative humidity established over saturated salt solutions at 25°C.

Lithium chloride	11.3%
Magnesium chloride	32.8%
Sodium chloride	75.3%
Potassium chloride	84.3%

A saturated salt solution may be placed inside the gas container, which after sufficient time produces a constant vapour pressure above the salt solution. Using different salt solutions makes it possible to study samples over a wide range of discrete, relative humidity. The effect of solutions on the vapour pressure is known from other solutions such as solutions containing sugar.
If the degree of humidity must be selected from a continuous range of humidity for the study of water vapour permeation an alternative method can be used.
Figure 4 illustrates a three-stage filling facility consisting of a lower part 170, a middle part 171 and an upper part 172 with the test sample 178. The lower part 170 contains a sufficient amount of water 177; the remaining inner volume of the lower part 170 is filled only with water vapour at the vapour pressure

of water vapour (100% relative humidity) that corresponds to the experimental conditions. Valve 174 is closed. The middle part 171 and the upper part 172 are under vacuum, which can be achieved by evacuating them with the valves 175 and 176 open. Then valves 175 and 176 are closed. Now valve 174 is opened and water vapour will stream from the lower part in the middle part. The amount of water vapour filling the middle part 171 comes from further evaporation of the water droplet 177. The original size of the water droplet 177 must be such that after filling the middle part 171 liquid water remains in the lower part 170. After some time the middle part 171 will be filled with water vapour at the vapour pressure of water vapour (100% relative humidity). Now valve 174 is closed and valve 175 opened. Water vapour streams from the middle part 171, which has the internal volume V_1 into the upper part 172, which has the volume V_2.
Because the same number of molecules is now occupying the volume V_1+V_2 instead of volume V_1, the pressure of the water vapour is reduced. In the absence of sinks, the resulting water vapour pressure will be $p=V_1*p_{fill}/(V_1+V_2)$ with p_{fill} the pressure the middle part 171 was filled with. The relative humidity in the upper part 172 will be $V_1/(V_1+V_2)$. The three parts 170, 171 and 172 may be detachable as a smaller size it is of advantage for the handling of the gas container in a vacuum chamber.
A coating of the interior of the parts 170, 171 and 172 of the gas container with a hydrophobic material may be advantageous. Using different isotopes of water such as $D_2{}^{16}O$, $D_2{}^{17}O$, $D_2{}^{18}O$, $H_2{}^{16}O$, $H_2{}^{17}O$, $H_2{}^{18}O$ for the water droplet 177 makes it possible to enhance the sensitivity of the mass spectrometric estimation because different isotopes have different backgrounds and using an isotope with a low background signal improves the signal to noise ratio.
The surface of body and lid may be coated with a moisture absorbing substance such as a metal (Ti, Al, etc.) or an oxide (CoO etc).

Concerning the **third aspect** of the invention an experiment may be carried out as follows:
The purpose of the experiment is, to measure the rate of permeation on samples other than simple films. Figure 5 a shows a representation of an assembly. The essential parts of the assembly are a gas container comprising a lower part 200 and an upper part 201. The test sample 202 is located between these two parts. Figure 5b shows in cross sectional view the interior 203 filled with the gas or vapour of interest. The filling may be done through a valve 204 similar to the procedures described in the first and second aspects of the invention. The gas or vapour enters the sample 202 through its inner edge 205, permeates through the sample and leaves it through its outer edge 206. The mass spectrometer 207 is located sufficiently close to a part of the outer edge to detect the permeated species. It is essential, that the lower part 200 and the upper part 201 have a much lower rate of permeation than the sample 202. The sample 202 may be a resin, such as an epoxy resin, which glues together the lower part 200 and the upper part 201.
Figure 5c shows the first alternative shape, where the sample 208 has the shape of a film. The gas or vapour enters the sample 208 through its faces 209, permeates through the sample 208 and leaves it through its edge 210 and is detected by the mass spectrometer 207. Valves 211 and 212 are provided for filling.
Figure 5d shows the second alternative shape, where the lower part 215, the sample 217 and the upper part 216 are located in an enclosure 220. The enclosure 220 is made of impermeable material. The space between the enclosure 220 on one side and the lower part 215, the sample 217 and the upper part on the other side, 221, is filled with the gas or vapour of interest. This can be done through a valve 223 similar to the procedures described in the first and second aspects of the invention. The gas or vapour enters the test sample 217 through the outer edges 224, permeates through the test sample and leaves it through inner edges 225. It then moves through the holes 218 and 219, which may be located close to the mass spectrometer 207.
Figure 5e shows the third alternative shape. This is very similar to the second alternative shape shown in figure 5d, except that the gas leaves the sample through its faces 227 rather than through its edges.
Figure 5f shows the fourth alternative shape comprising a circular or ring shaped sample 229. Such a sample can be rotated on a suitable sample holder; such an experiment is of interest in the position-resolved mode (see fourth aspect of the invention).
Figure 5g shows the fifth alternative shape, where the sample is hemispherical. Figure 5h shows the fifth alternative shape in cross sectional view. The hemispherical test sample 230 is mounted on a base 231 and covered by an enclosure 232. It is essential, that the base 231 and the enclosure 232 have a significantly lower rate of permeation than the sample 230. Preferably they are made of an impermeable material such as a metal. The space between the sample 230 and the enclosure 233 is filled with a gas or vapour of interest, which may be done through a valve 234. The gas or vapour enters the sample 230 on its outer side, permeates through the sample 230 and leaves it on its inner side. The gas or vapour then

moves through a hole 235, which is located sufficiently close to the mass spectrometer 207, where the gas or vapour species are detected.

Concerning the **fourth aspect** of the invention an experiment may be carried out as follows:
The purpose of the experiment is to measure the rate of permeation on different locations on a test sample.
Figure 6a shows an arrangement, where the gas container 250 with the test sample 251 and the mass spectrometer 257 are contained in a vacuum chamber 256, which is evacuated through a port 261. The gas or vapour contained in the gas container 250 permeates through the test sample 251 and enters the ionisation region 252 of the mass spectrometer 257. The ions are then travelling on a trajectory through the quadrupoles 253 and selected ions are counted in the detector 254. Although other types of mass spectrometers may be suitable too the quadrupole mass spectrometers are widely used because of their ease of use. Without an enclosure, gas or vapour from a wide area of the sample 251 may contribute to the signal in the detector 254. The area, where gas or vapour is allowed to enter the mass spectrometer, can be reduced by fitting an enclosure 255 around the mass spectrometer. The enclosure is preferable of cylindrical shape with a small hole 258, typically 1 mm in diameter or less, in the bottom 259. If the distance between the test sample 251 and the bottom 259 is sufficiently small and the hole 258 is facing the sample 251, position resolved permeation measurements could be carried out by moving the gas container 250 with the sample 251 relative to the mass spectrometer 257. The movement can be accomplished by means of a xyz-stage 7 (see figure 1) where the gas container is attached to after transfer of the test sample into the investigation chamber 2. Another possibility is to mount the mass spectrometer to such a xyz-stage and move it. To keep a sufficient low vacuum level inside the enclosure 255, a port 260 is provided, which can either be connected to a separate pump or can be connected through a suitable adapter to the main pump 11 (see figure 1).
Figure 6b shows the first alternative shape of the enclosure, where a small tube 270 is attached to the bottom 259 of the enclosure. Figure 6c shows the second alternative shape of the enclosure, where the bottom of the enclosure 271 is of conical shape. Figure 6d shows the third alternative shape, where a conical bottom of the enclosure 255 has a small tube 272 attached to it.
Figures 6 e, f and g illustrate how the shape to the bottom of the enclosure and the attachment of a tube 270 to the bottom 259 with a hole 258 (see corresponding figures 6a, b and c) influences the probability of a gas molecule, which originates from a certain area of the surface of the test sample, entering the mass spectrometer. The vacuum chamber is under a level of vacuum, where collisions of gas molecules with parts of the vacuum system such as wall have a higher probability of occurrence than collisions between gas molecules. This is certainly the case below a pressure of $1x10^{-7}$ mbar.
Figure 6e shows a flat bottom 259 of the enclosure 255 with a hole 258 facing a test sample 251. A molecule originating from location 281 in the direction indicated goes straight through the hole 258 into the mass spectrometer. A molecule originating from location 280 in the direction indicated may travel as follows: it will hit the enclosure, travel back hitting the sample etc. eventually entering the mass spectrometer through the hole 258. Figure 6f shows that by attaching a tube 270 the probability of molecules originating at the same location 280 and in the same direction as shown in figure 6e entering the mass spectrometer through the hole 258 will be reduced. Figure 6g shows that by using a conically shaped bottom 271 the probability of molecules originating at the same location 280 and in the same direction as shown in figure 6e entering the mass spectrometer through the hole 258 will be reduced.
The biggest reduction of the probability of molecules originating at the same location 280 and in the same direction as shown in figure 6g entering the mass spectrometer through the hole 258 will be achieved by attaching a tube to a conically shaped bottom (figure 6d). In this case, the area of the test sample, where gas or vapour entering the mass spectrometer originates, is minimized. Optimising the gas container and the enclosure of the mass spectrometer can further reduce the amount of gas or vapour entering the mass spectrometer from unwanted regions. Figure 6h shows the fourth alternative shape, where a small tube 273 is attached to the bottom 259 of the enclosure. The shape of the tube is such, that in connection with using a gas container similar to the shape shown in figure 3q, where the diameter of the tube 273 and the diameter of the holes 138 in the lid of the gas container 137 are chosen as to minimizing the amount of gas entering the mass spectrometer 257 from a region other than the hole 138.
Figure 6i shows the fifth alternative shape, where the conical bottom of the enclosure 255 has a small tube 274 attached to it. The shape of the tube and the conically shaped bottom is such, that in connection with using a gas container similar to the shape shown in figure 3q, where the diameter of the tube 273 and the diameter of the holes 138 in the lid 137 of the gas container 139 are chosen as to minimizing the amount of gas entering the mass spectrometer 257 from a region other than the hole 138.
Due to the emission of the filaments, the enclosure 255 of the mass spectrometer 257 may become hot and therefore cooling may be necessary. Figure 6j shows a shape, where tubes 257 are attached to the

enclosure 255. The tubes 257 get into the vacuum chamber through a liquid feedthrough 256. The tubing 257 is in physical contact with the enclosure 255. If a coolant (i.e. a coolant such as water or liquid nitrogen) with a temperature below the temperature of the enclosure 255 is circulated through the tubes 257, heat will be removed from the enclosure 255 by the coolant.
Figure 6k shows the first alternative shape of the cooling device. One end of a piece of material 259, with a high thermal conductivity, for example copper, is attached to the enclosure 255 or to a sleeve 258, which is located around the enclosure. The other end of the piece of material 259 is connected to a feedthrough 260, which also has a high thermal conductivity. Heat may now be conducted from the enclosure 255 with the sleeve 258 through the piece of material 259 and the feedthrough 260 to the exterior of the vacuum chamber. There the heat can be carried away by conventional means such as a water bath.
The filling procedure and the sample transfer can be done similar to what is described in the first and second aspects of the invention.
Different shapes of the gas containers were explained above and examples are shown in figure 3. A gas container as shown in figure 3v and x is particularly useful for position resolved permeation measurements. Figure 3v shows the test sample 151 mounted between the body 150 and the lid 153. Figure 3x shows a top view of the lid 153. It contains a number of holes 156 separated by a distance of a fraction of a mm or a few mm. The gas container is then positioned very close to the mass spectrometer, for example similar to the arrangement shown in figures 6h and i for the measurement. After finishing the measurement at one location (for one hole), the sample can be shifted relative to the mass spectrometer for the mass spectrometer to face the next hole. This way, the rate of permeation can be measured along a line. Alternative shapes for a gas container, which can be used to obtain the rate of permeation from a two-dimensional area, are shown in figures 3m, n, o and p. The positioning of the gas container and its movement along a line or along several lines relative to the mass spectrometer can be done with a manually operated or a motorized xyz-stage.
Figure 6l shows a diagrammatic view of a test sample with areas of different rates of permeation. Area 290 has a rate of permeation P_1 and area 291 has a different rate of permeation P_2. Possible applications comprise studying devices, which deliver drugs to a wound. In the case of $P_1>P_2$ where the centre of the wound needs a bigger amount of the drug than the edge, the measurement of the rate of permeation would give a higher value for the centre 290 compared to the edge 291.
Figure 6m shows a device, where parts of the surface or parts stretching through the entire thickness of the test sample are made of a material 292 with the rate of permeation P_2. The surrounding 293 has the rate of permeation P_1. The gas or vapour is now forced to travel along the pathway indicated in figure 6p. The advantage of the current invention is that it enables the position resolved testing of such a device.
Another device is shown in figure 6n. A very small area 294 of diameter of a few mm or less has a rate of permeation P_1, which is greater than the rate of permeation P_2 of the surrounding 295 ($P_1>>P_2$). The advantage of such a device is, that a defined amount of gas can be delivered to awkward locations, where the supply of a gas or a vapour by other means such as a pipe is cumbersome. The advantage of the current invention is that it enables the position resolved testing of such kind of devices.

Concerning the **fifth aspect** of the invention an experiment may be carried out as follows:
The purpose of the experiment is to measure the temperature of the test sample.
Figure 7a shows an example how to arrange the detector and the test sample for a temperature measurement. A test sample 280 is mounted to the gas container 281. The gas container has a bottom 282, which is transparent for the wavelength, where the radiation 283 emitted from the test sample 280, has sufficient intensity for detection. A pyrometer or infrared detector 285 is positioned outside the vacuum chamber 287 containing the mass spectrometer 288 and focussed on the test sample 280. Because the test sample 280 is inside the vacuum chamber and the pyrometer detector is outside the chamber, a view port 284 is needed, which is transparent for the wavelength, where the radiation 283 emitted from the test sample 280 has sufficient intensity for detection (maximum of intensity preferred).
Figure 7b shows the first alternative shape of the gas container for temperature measurement by means of a pyrometer. The entire body 286 of the gas container is made of a material, which is transparent for the wavelength, where the radiation 283 emitted from the test sample 280 has sufficient intensity for detection (maximum of intensity preferred).
The material for the bottom of the viewport 282, the body of the gas container 286 and the material for the viewport 284 must be selected according to the emission characteristic of the specific test sample.

Claims

First aspect

1.1. A method of measuring the rate of permeation of vapours or gases or mixtures thereof through a test sample either integral or position-resolved comprising:
- Providing an amount of vapour or gas in a gas container at a certain vapour or gas pressure;
- Arranging the container containing the vapour or the gas in a vacuum chamber, which is under vacuum such that the vapour or gas permeating from the container through the test sample communicates with the vacuum chamber under vacuum
- Providing a means to change the relative position between the gas container with the test sample and the mass spectrometer
- Using a mass spectrometer to detect the partial pressure of the gas or vapour after permeation through the test sample
- Estimating the rate of permeation from the signal measured by the mass spectrometer

1.2. A method as claimed in Claim 1.1 wherein the gas container comprises a body, to which one or more test samples are attached forming a seal.

1.3. A method as claimed in Claim 1.2 wherein one or more of the remaining openings of th ebody of the gas container are used to house a closing device such as a valve to separate the interior of the gas container from the outside.

1.4. A method as claimed in Claim 1.2 wherein the test sample is sealed to the gas container by pressing the test sample against a sealing face of the gas container without using a gasket

1.5. A method as claimed in claim 1.2 wherein the test sample is sealed to the gas container by pressing the test sample against a sealing face of the gas container using a gasket.

1.6. A method as claimed in claim 1.2 wherein the sealing areas of the test sample and/or the container body are coated with or made of a vapour or gas absorbing material.

1.7. A method as claimed in claim 1.2 wherein the test sample is sealed to the gas container by an adhesive

1.8. A method as claimed in claim 1.2 wherein the test sample is a film

1.9. A method as claimed in claim 1.2 wherein the test sample consists of a stack of materials.

1.10. A method as claimed in claim 1.2 where the gas container has an increased ratio of volume to test sample area.

1.11. A method as claimed in claim 1.2 where the gas container is made of the test sample material.

1.12. A method as claimed in claim 1.11 where a part of the gas container has a reduced thickness for locally increased permeation

1.13. A method as claimed in claim 1.11 where the gas container is coated with an impermeable material or a material of much lower rate of permeation

1.12. A method as claimed in claim 1.2 where the gas container has a lid with a supporting structure

1.13. A method as claimed in claim 1.2 where the gas container has a movable part for changing the internal volume of the gas container.

1.14. A method as claimed in claim 1.2 where the gas container is made of a piezoelectric material.

1.15. A method as claimed in claim 1.2 where the gas container contains a capacitive sensor for internal pressure measurement

1.16. A method as claimed in claim 1.2 where the gas container has a lid with parallel faces having holes extending through the lid.

1.17. A method as claimed in claim 1.1 where the gas container is filled with gas or vapour inside a vacuum chamber

1.18. A method as claimed in claim 1.17 where the gas container is filled through a hole with a closing device inside a vacuum chamber by filling the entire vacuum chamber with gas or vapour.

1.19. A method as claimed in claim 1.17 where the closing device is handled by means of a feedthrough with or without a flexible part attached to it.

1.20. A method as claimed in claim 1.17 where the gas container is filled directly from a gas reservoir containing gas or vapour.

1.21. A method as claimed in claim 1.17 where the gas container is connected to a gas or vapour reservoir by means of a tube during filling.

1.22. A method as claimed in claim 1.2 where the gas or vapour pressure inside the gas container can be changed

1.23. A method as claimed in claim 1.2 where the temperature of the gas container with the test sample is changed by cooling or heating over a wide range, including cryogenic temperatures.

1.24. A method as claimed in claim 1.2 wherein the test sample is made of a polymer, a metal, a ceramic, a biological material or a combination thereof.

1.25. A method as claimed in claim 1.1 where the partial pressure is measured with the mass spectrometer after the signal has stabilised to a constant value.

1.26. A method according to claim 1.1 where the rate of permeation of a gas or vapour is determined from the partial pressure (measured by a mass spectrometer) and calibration against the rate of permeation of gas or vapour of reference samples.

1.27. A method according to claim 1.26 where the partial pressure measured from the reference samples is used for calibration

1.28. A method according to claim 1.26 where the total pressure measured from the reference samples is used for calibration.

1.29. A method according to claim 1.1 where the rate of permeation of a gas or vapour through a test sample is determined from the partial pressure (measured by a mass spectrometer) and calibration against a calibrated gas leak is used for calibration.

1.30. A method according to claim 1.1 where the experiment is carried out in an high vacuum (HV) chamber under vacuum.

1.31. A method according to claim 1.1 where the experiment is carried out in an ultra-high vacuum (UHV) chamber under vacuum.

1.32. A method according to claim 1.1 where the experiment is carried out in an extra-high vacuum (XHV) chamber under vacuum.

1.33. A method according to claim 1.1 where the effective permeation area of the test sample is a few mm to few cm in one or two dimensions or less.

Sec nd aspect

2.1. A method according to claim 1.1 where the vapour is water vapour.

2.2. A method of measuring the rate of permeation of water vapour through a test sample comprising:
-Providing an amount of water vapour in a container at a certain relative humidity;

-Arranging the container containing the water vapour in a vacuum chamber under vacuum such that the water vapour permeating through the test sample communicates with the vacuum chamber under vacuum
- Providing a means to change the relative position between gas container with test sample and the mass spectrometer
-Using a mass spectrometer to detect the partial pressure of the water vapour after permeation of the water vapour through the test sample;
-Deriving the rate of water vapour permeation from the signal measured by the mass spectrometer

2.3. A method as claimed in claim 2.1 wherein the gas container comprises a body, to which one or more test samples are attached forming a seal and the test sample(s) are covering openings of the body of the gas container.

2.4. A method as claimed in claim 2.2 wherein one or more of the remaining openings are used to house a closing device such as a valve to separate the interior of the gas container from the outside.

2.5. A method as claimed in claim 2.2 wherein the test sample is sealed to the gas container by pressing the gas container against a sealing face of the gas container without using a gasket

2.6 A method as claimed in claim 2.2 wherein the test sample is sealed to the gas container by pressing the gas container against a sealing face of the gas container and using a gasket.

2.7. A method as claimed in claim 2.2 wherein the sealing areas of the test sample and/or the container body are coated or made of a vapour or gas absorbing material.

2.8. A method as claimed in claim 2.2 wherein the test sample is sealed to the gas container by an adhesive

2.9. A method as claimed in claim 2.2 wherein the test sample is a film

2.10. A method as claimed in claim 2.2 wherein the test sample consists of a stack of materials.

2.11. A method as claimed in claim 2.2 where the gas container has an increased ration of volume to test sample area.

2.12. A method as claimed in claim 2.2 where the gas container is made of the test sample material.

2.13. A method as claimed in claim 2.12 where the gas container has a thinner part for increased permeation

2.14. A method as claimed in claim 2.11 where the gas container is coated with a material of much lower rate of permeation

2.15. A method as claimed in claim 2.2 where the gas container has a lid with a supporting structure

2.16. A method as claimed in claim 2.2 where the gas container has a movable part for changing the internal volume.

2.17. A method as claimed in claim 2.2 where the gas container is made of a piezoelectric material.

2.18. A method as claimed in claim 2.2 where the gas container contains a capacitive sensor for internal pressure measurement

2.19. A method as claimed in claim 2.2 where the gas container has a lid with parallel faces having holes extending through the lid.

2.20. A method as claimed in claim 2.1 where the gas container is filled with water vapour inside a vacuum chamber

2.21. A method as claimed in claim 2.20 where the gas container is filled through a hole with a closing device inside a vacuum chamber by filling the entire vacuum chamber with water vapour.

2.22. A method as claimed in claim 2.20 where the closing device is handled by means of a feedthrough with or without a flexible part attached to it.

2.23. A method as claimed in claim 2.20 where the gas container is filled from a reservoir containing water vapour.

2.24. A method as claimed in claim 2.20 where the gas container is connected to a water vapour reservoir by means of a tube during filling.

2.25. A method as claimed in claim 2.2 where the water vapour pressure can be changed.

2.26. A method as claimed in claim 2.2 where the temperature of the gas container with the test sample is changed by cooling or heating over a wide range, including very low temperatures.

2.27. A method as claimed in claim 2.2 wherein the test sample is made of a polymer, a metal, a ceramic, a biological material or a combination thereof

2.28. A method as claimed in claim 2.1 where the partial pressure is measured with the mass spectrometer after the signal has stabilised to a constant value.

2.29. A method according to claim 2.1 where the rate of permeation of water vapour is determined from the partial pressure (measured by a mass spectrometer) and calibration against the rate of permeation of water vapour of reference samples.

2.30. A method according to claim 2.29 where the partial pressure of water measured from the reference samples is used for calibration

2.31. A method according to claim 2.29 where the total pressure measured from the reference samples is used for calibration.

2.32. A method according to claim 2.1 where the rate of permeation of water vapour is determined from the partial pressure (measured by a mass spectrometer) and calibration against a calibrated gas leak is used for calibration.

2.33. A method according to claim 2.1 where the experiment is carried out in an ultra-high vacuum (UHV) chamber under vacuum or in a extra-high vacuum (XHV) chamber under vacuum or in a high vacuum (HV) chamber under vacuum .

2.34. A method according to claim 2.1 where the effective permeation area of the test sample is a few mm to few cm in one or two dimensions or less.

2.35. A method as claimed in claim 2.2 where the gas container contains a salt solution, which produces a certain relative humidity, which is characteristic for the salt solution, inside the gas container.

2.36. A method as claimed in claim 2.2 where the signal to noise ratio of the signal detected by the mass spectrometer is reduced by choosing a suitable isotope from $D_2{}^{16}O$, $D_2{}^{17}O$, $D_2{}^{18}O$, $H_2{}^{16}O$, $H_2{}^{17}O$, $H_2{}^{18}O$.

2.37. A method according to claim 2.1 where the rate of water vapour permeation is determined from the partial pressure (measured by a mass spectrometer) and calibration against the partial pressure against one or more samples with a known rate of water vapour permeation.

2.38. A method as claimed in claim 2.2 where a three-stage gas container-assembly is used to introduce water vapour at a chosen relative humidity into the gas container.

2.39. A method as claimed in claim 2.38 where the three stages of the gas container are connected and can be separated by valves.

2.40. A method as claimed in claim 2.38 where one stage of the gas container contains liquid water.

2.41. A method as claimed in claim 2.38 where one stage of the gas container contains water vapour at 100% humidity but no liquid water.

2.42. A method as claimed in claim 2.38 where one stage of the gas container contains water vapour at the desired relative humidity.

2.43. A method according to claim 2.1, where the interior of the gas container is coated with a hydrophobic substance.

Third aspect

3.1. A method according to claim 1.1 where the permeation measurement is carried on a test sample other than a film

3.2. A method according to claim 3.1 where the test sample comprises a body of less permeable material and another region of a material which permits a higher rate of permeation.

3.3. A method according to claim 3.1 where the test sample is hollow.

3.4. A method according to claim 3.1 where the gas container is the test sample

3.5. A method according to claim 3.1 where the test sample is contained in an enclosure keeping gas or vapour between the test sample and the enclosure.

3.6. A method according to claim 3.5 where the test sample or the enclosure have a hole, through which the permeated gas or vapour can communicate with the mass spectrometer.

3.7. A method according to claim 3.2 where the test sample is a stack of films or a composite and the edges of the test sample have a rate of permeation, which is significantly different from the rate of permeation through the upper or lower faces of the stack of films.

3.8. A method according to claim 3.3 where the test sample contains the gas or vapour of interest.

3.9. A method according to claim 3.8 where the test sample is filled with gas or vapour through a filling facility such as a valve.

3.10. A method according to claim 3.1 where the test sample is an amount of resin between two parts of the gas container.

3.11. A method according to claims 1.1 and 2.1 where the rate of permeation through an edge is measured.

3.12. A method according to claims 1.1 and 2.1 where the rate of permeation in-plane is measured.

Fourth aspect

4.1. A method according to claim 1.1 where the permeation measurement is carried out on different locations on the test sample.

4.2. A method according to claim 2.1 where the permeation measurement is carried out on different locations on the test sample.

4.3. A method according to claim 4.1 where the test sample is moved with respect to the mass spectrometer.

4.4. A method according to claim 4.1 where the mass spectrometer is moved with respect to the test sample.

4.5. A method according to claim 4.1 where the rate of permeation is measured at individual points of the test sample

4.6. A method according to claim 4.1 where the mass spectrometer is covered in an enclosure

4.7. A method according to claim 4.6 where the enclosure has a hole through which the gas enters the mass spectrometer after permeation through the test sample

4.8. A method according to claim 4.6 where the enclosure has a shape as to reduce or eliminate the amount of gas that enters the mass spectrometer from unwanted areas of the test sample.

4.9. A method according to claim 4.6 where the enclosure has a flat bottom with a hole.

4.10. A method according to claim 4.6 where the enclosure has a flat bottom with a hole and a tube attached to the hole.

4.11. A method according to claim 4.6 where the enclosure has a conical bottom with a hole.

4.12. A method according to claim 4.6 where the enclosure has a conical bottom with a hole and a tube attached to the hole.

4.13. A method according to claim 4.1 where the gas container has a shape as to reduce or eliminate the amount of gas that enters the mass spectrometer from unwanted areas

4.14. A method according to claim 4.1 where the gas container has a lid with parallel face and holes extending through the whole thickness of the lid.

4.15. A method according to claim 4.6 where the enclosure housing the mass spectrometer is evacuated by a separate pump or through a bypass to the existing pump on the vacuum chamber.

4.16. A method according to claim 4.1 where the gas container contains a liquid or a solid.

Fifth aspect

5.1. A method according to claim 1.1 where the temperature of the test sample is determined by detecting the radiation, in particular the infrared radiation, emitted from the test sample.

5.2. A method according to claim 5.1 where the temperature of the test sample is determined at different locations on the test sample.

5.3. A method according to claim 5.1 where the vacuum chamber contains a viewport made of a material that transmits the relevant part of the emission spectrum from the test sample.

5.4. A method according to claim 5.1 where the bottom of the gas container is made of a material that is transparent for the relevant part of the spectrum emitted from the test sample.

5.5. A method according to claim 5.1 where the large parts or the entire gas container are made of a material that is transparent for the relevant part from the emission spectrum of the test sample.

Apparatus

6.1. An apparatus for measuring the rate of permeation of a gas or vapour (including water vapour) consisting of:
- one or more vacuum chambers
- a gas container which is removable from the vacuum system
- a filling facility
- a mass spectrometer (for partial pressure measaurement)
- a means for changing the relative positions of mass spectrometer and test sample
- a means of transferring the gas container with the test sample.

6.2. The apparatus according to claim 6.1 having a gas container that can be filled by means of a filling facility provided in one of the vacuum chambers.

6.3. The apparatus according to claim 6.1 with the investigation chamber is under HV, UHV or XHV conditions.

6.4. The apparatus according to claim 6.1 where a mechanical support is provided to support the test sample.

6.5. The apparatus according to claim 6.1 where the gas container can be moved between vacuum chambers and removed from the vacuum chambers.

6.6. The apparatus according to claim 6.1 where the size of test sample is less than a mm to a few mm in one or two dimensions.

6.7. The apparatus according to claim 6.1 where the test sample is clamped or glued to the gas container

6.8. The apparatus according to claim 6.1 where the test sample is a film or a device or an assembly of several parts of a device.

6.9. The apparatus according to claim 6.1 where the gas container contains gas or vapour including water vapour.

6.10. The apparatus according to claim 6.9 where the pressure of the gas or vapour inside the gas container can be varied.

6.11. The apparatus according to claim 6.1 where the temperature of the test sample can be measured by detecting radiation emitted from the test sample

6.12. The apparatus as claimed in claim 6.1 where the partial pressure is measured with the mass spectrometer after the signal has stabilised to a constant value.

6.13. The apparatus as claimed in claim 6.1 where the partial pressure is measured with the mass spectrometer where the initial partial pressure is extrapolated from a decreasing partial pressure caused by depletion of the gas or vapour in the gas container.

6.14. The apparatus according to claim 6.1 where the rate of permeation is estimated from the measured partial pressure and a calibration against one or more samples with a known rate of permeation.

6.15. The apparatus according to claim 6.1 where the temperature of the test sample can be varied.

6.16. The apparatus according to claim 6.1 where the gas container comprises a mechanical support for the test sample, which can be used to improve the heat transfer to and from the test sample.

6.17. An apparatus according to claim 6.1 where the mass spectrometer has an enclosure.

6.18 An apparatus according to claim 6.17 where the enclosure has a cooling facility.

Abstract

A method and an apparatus are provided for measuring the rate of permeation of a gas or vapour or a mixture thereof through a test sample using a mass spectrometer as detector. The test sample covers a hole in a gas container, through which the test sample is exposed to the gas or vapour. The test sample may be embodied as the gas container itself. The gas container is filled with a gas or vapour inside a filling chamber. After transferring the test sample to the investigation chamber the partial pressure of the gas or vapour of interest is detected after permeation through the test sample. After calibration the measured partial pressure is converted into the rate of permeation. The rate of permeation can either be measured as integral quantity over an area of the test sample or position-resolved at different locations of the test sample.

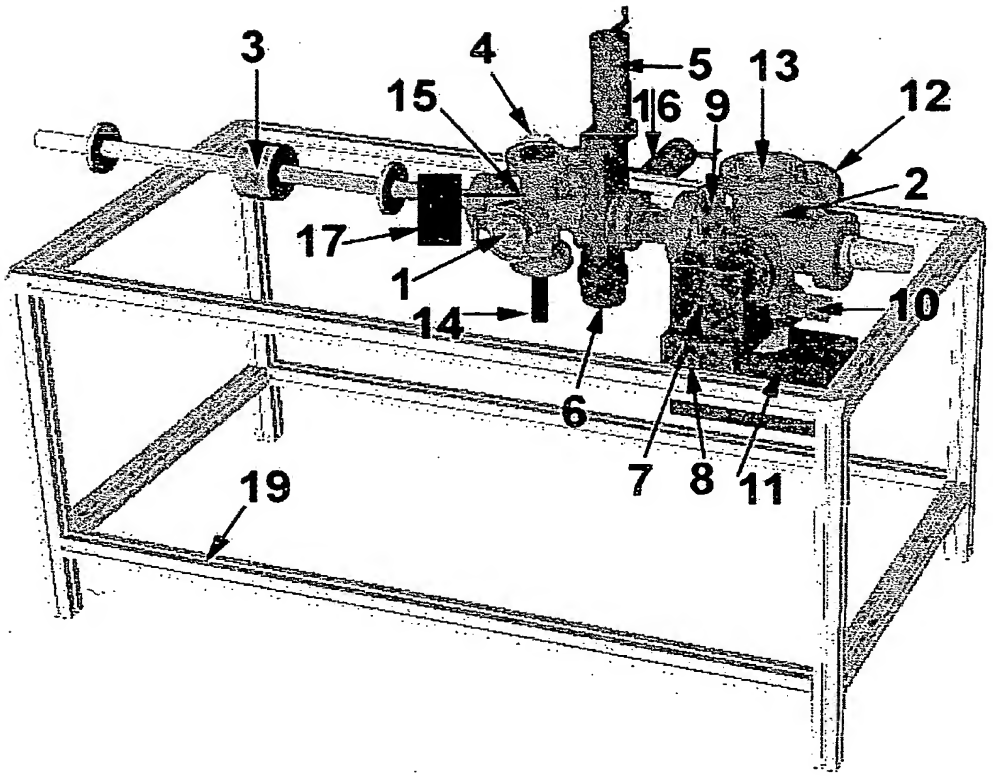
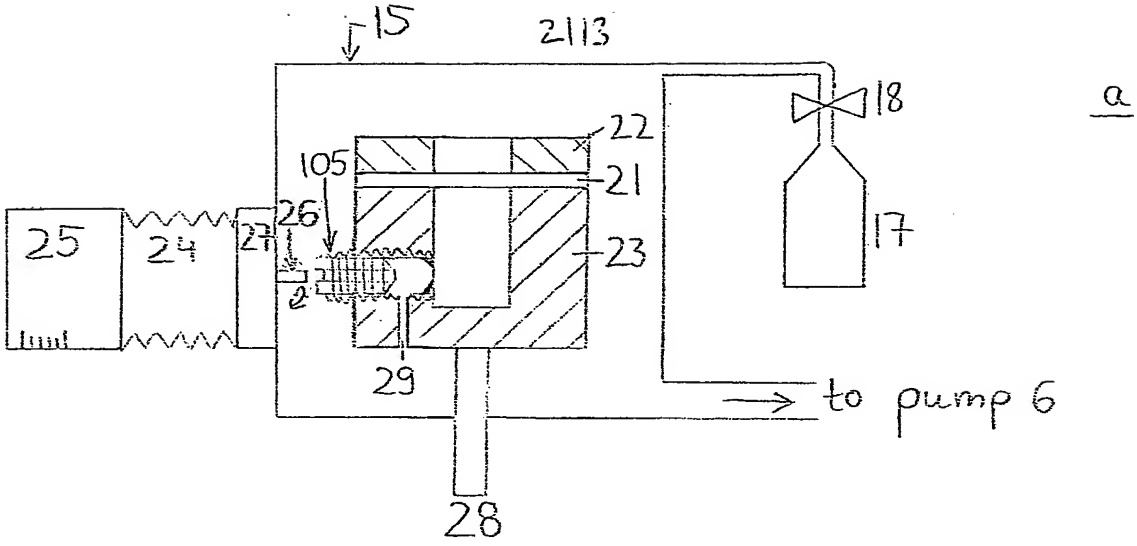


FIG. 1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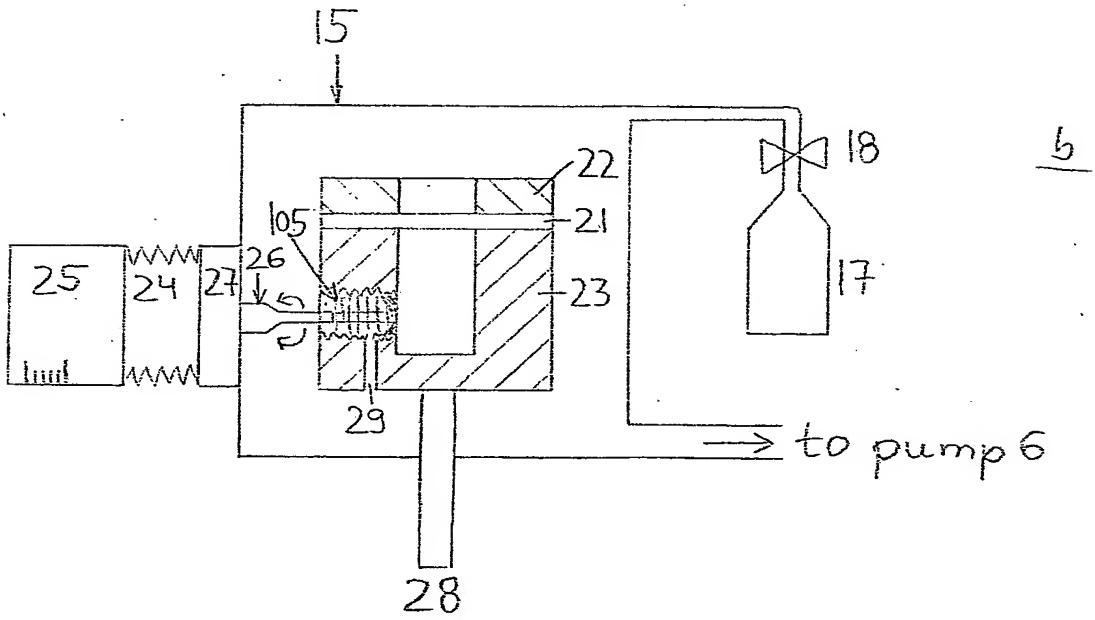
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b

FIG. 2

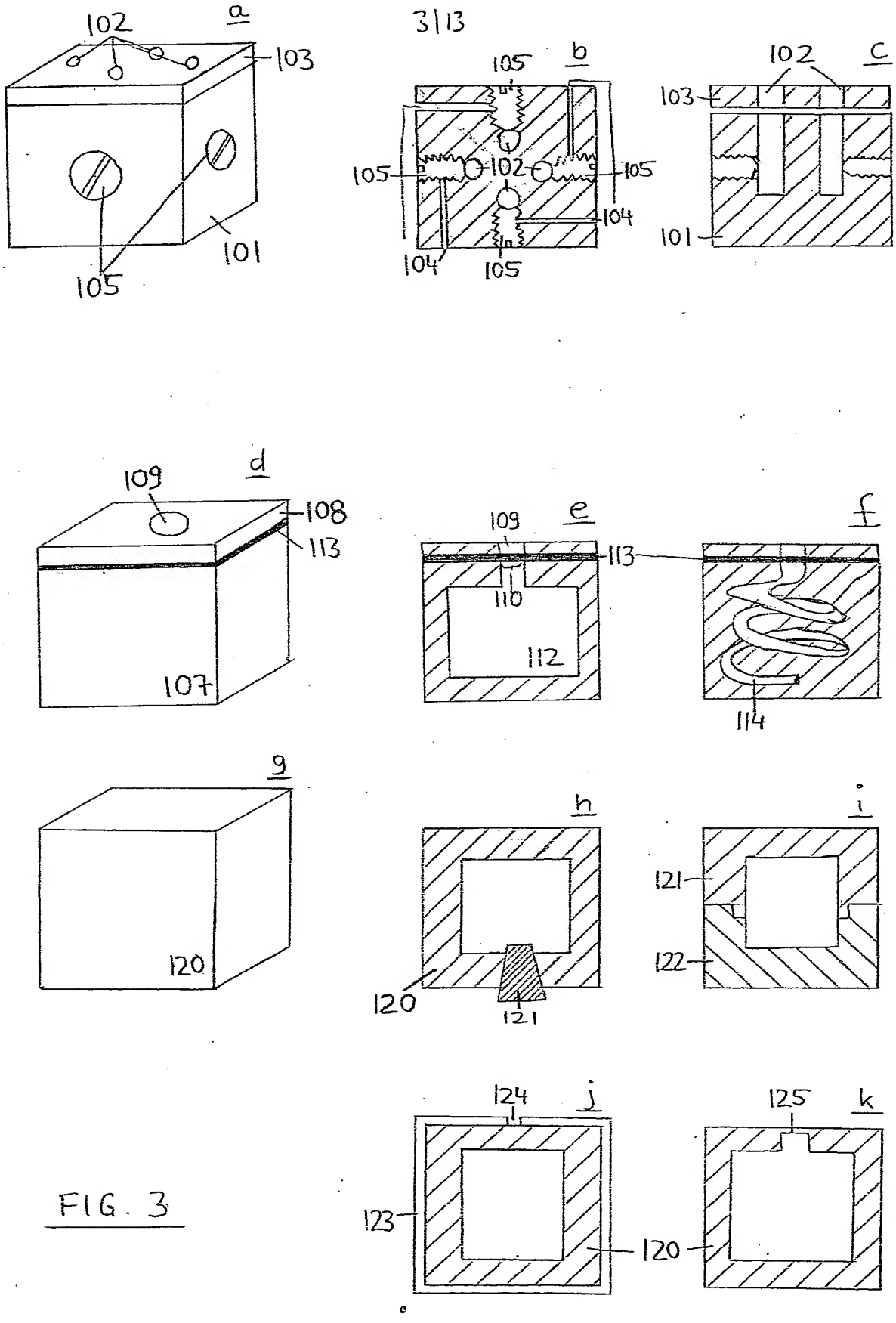
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FIG. 3

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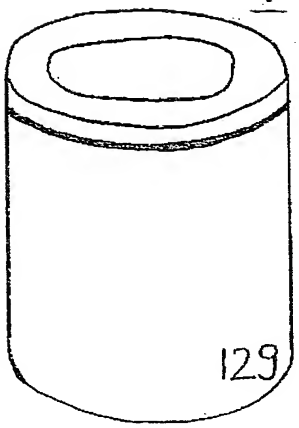

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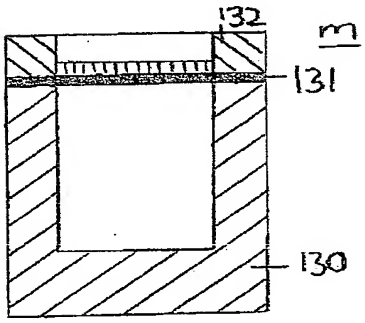

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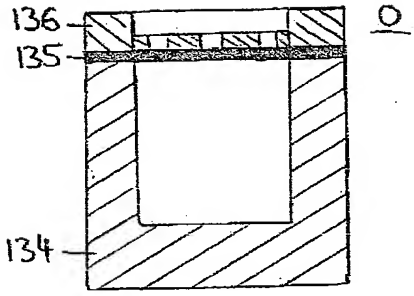

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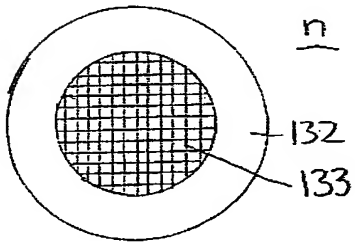

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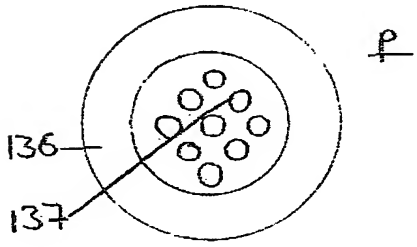

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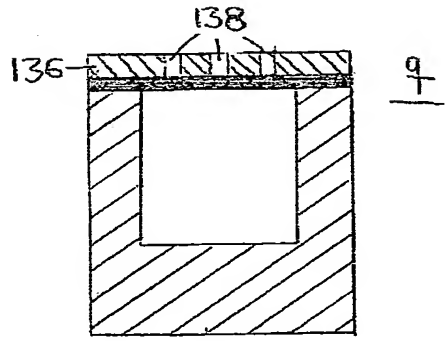

FIG. 3
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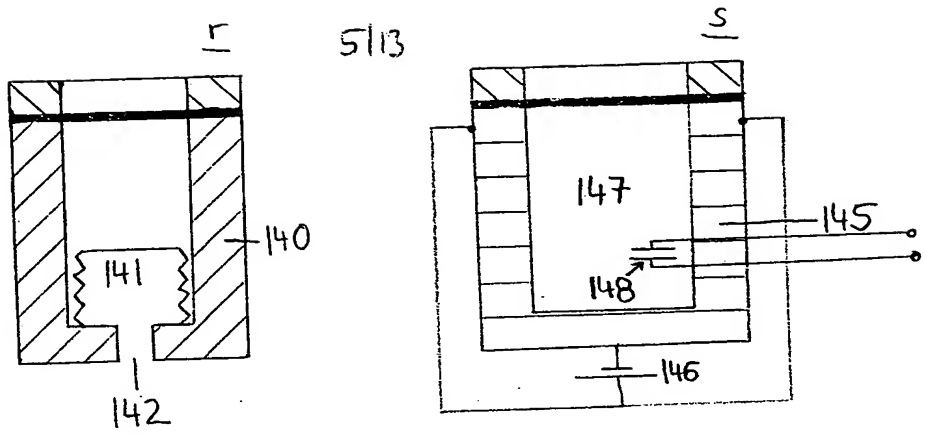

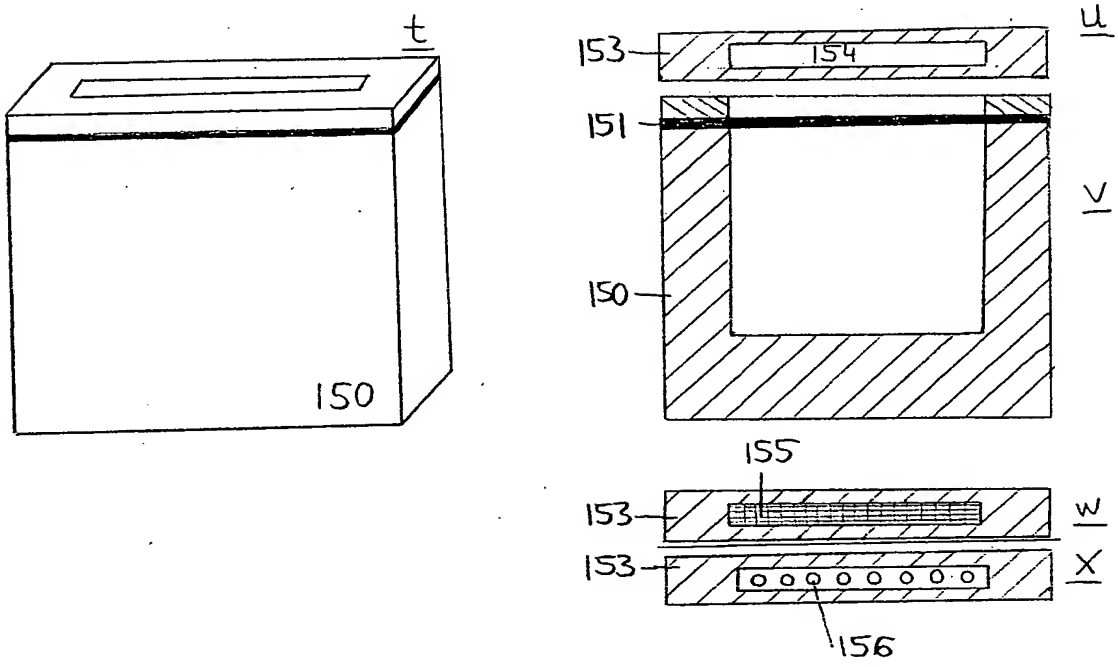

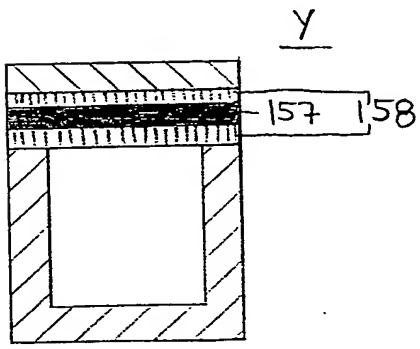

FIG. 3
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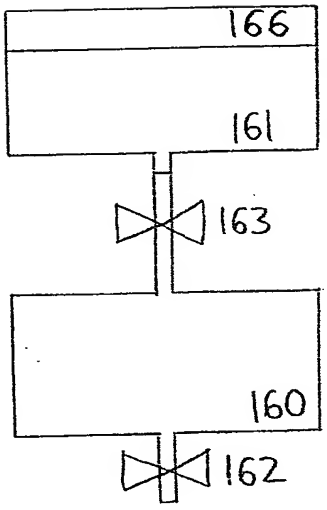

FIG 4a

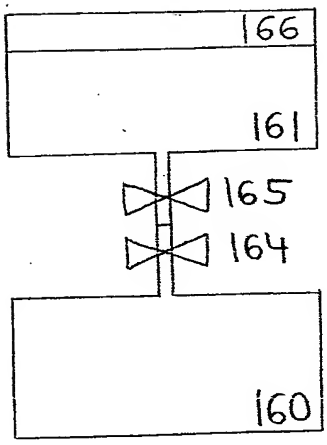

FIG 4b

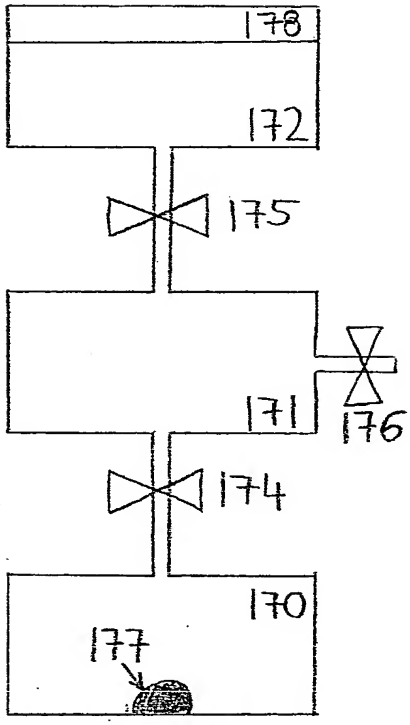

FIG. 4C

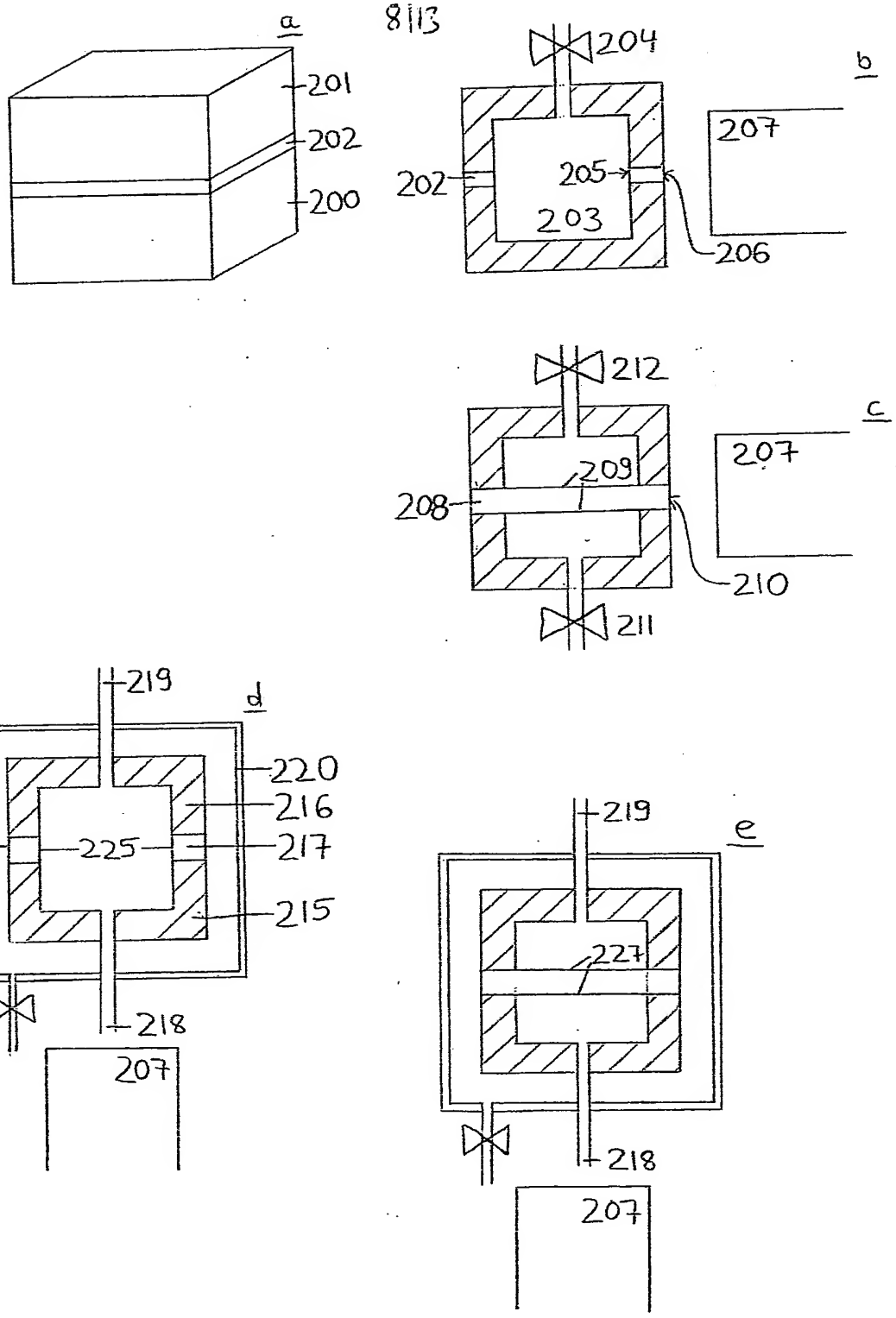
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FIG. 5

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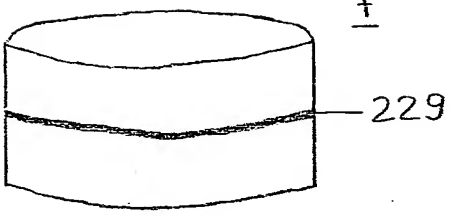

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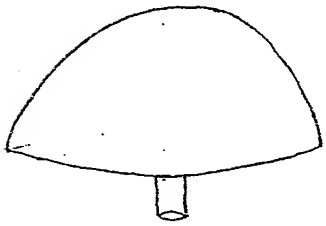

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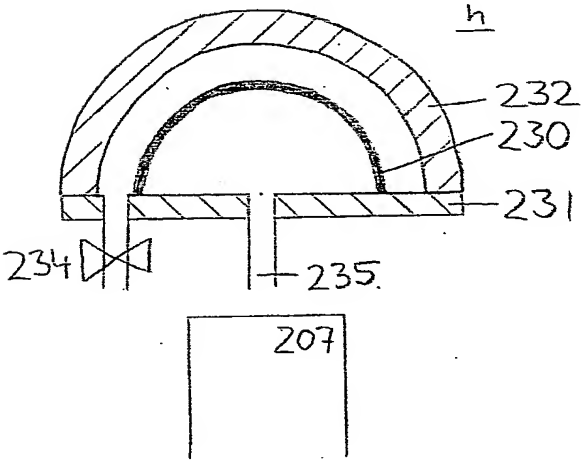

FIG. 5
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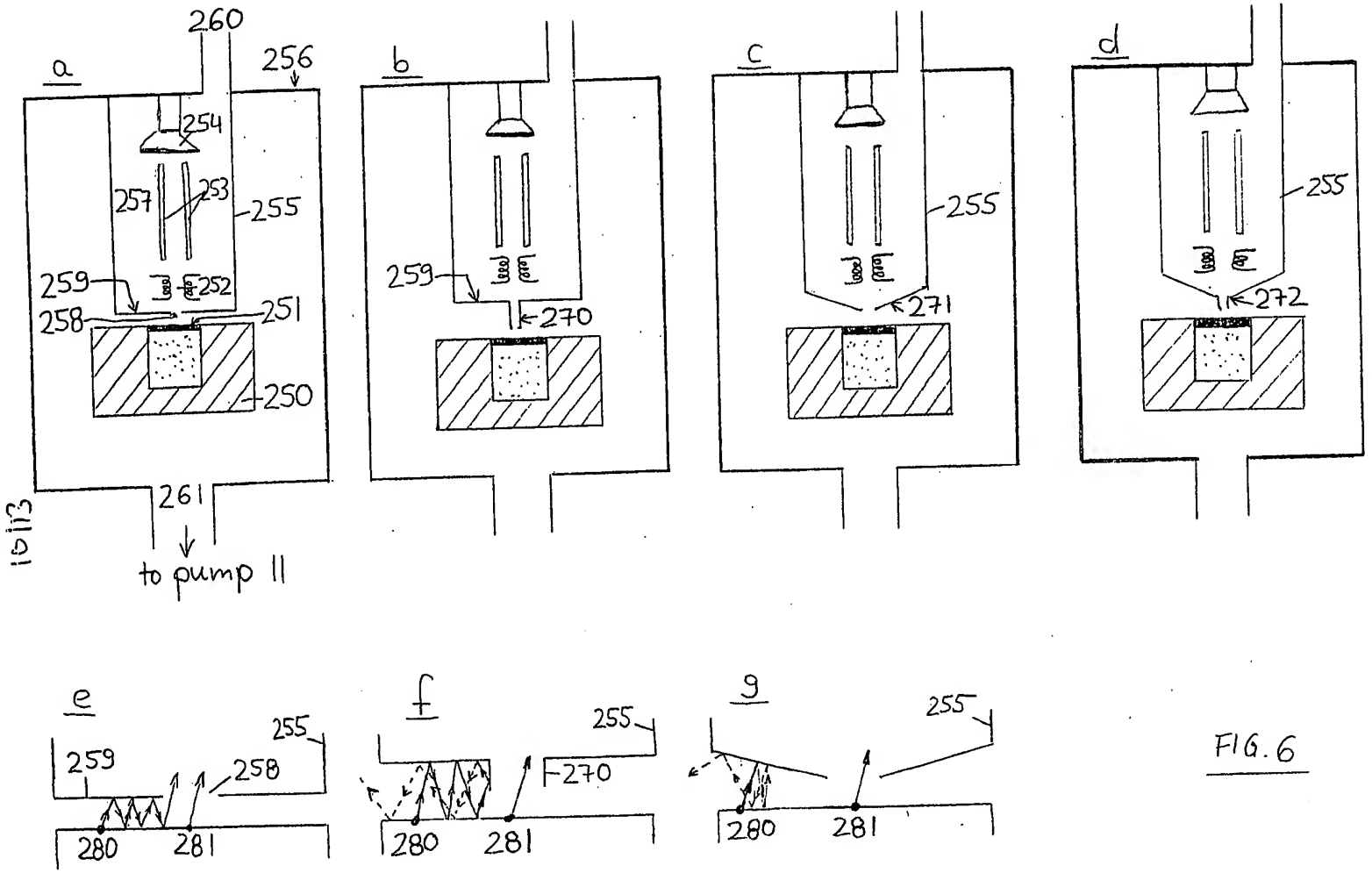
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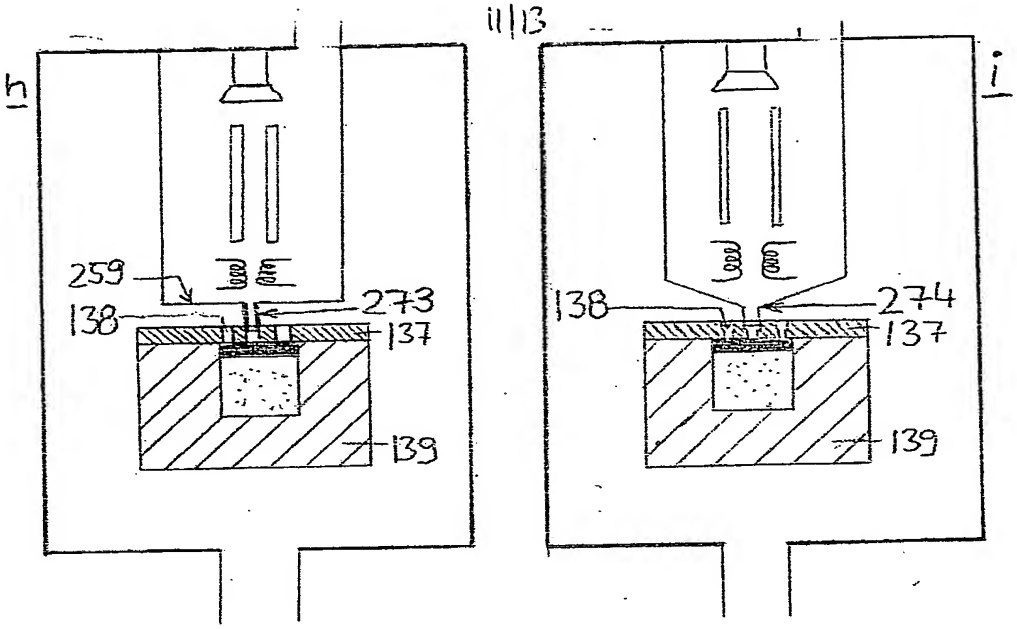
FIG. 6



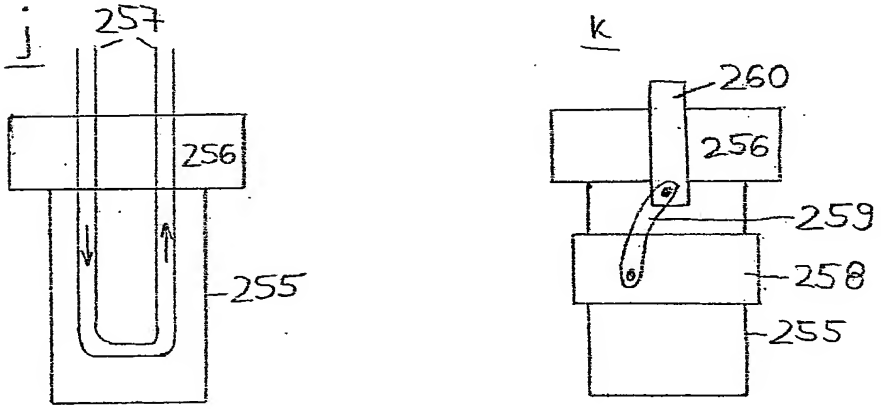


FIG. 6
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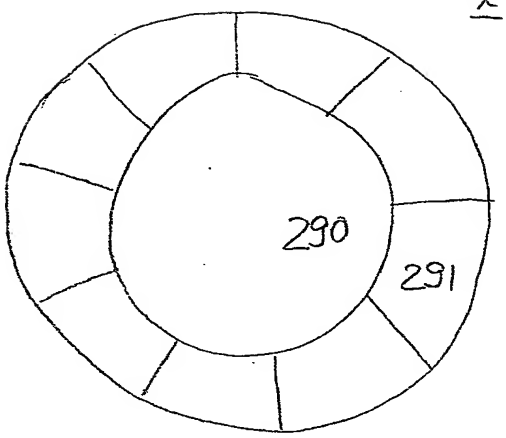

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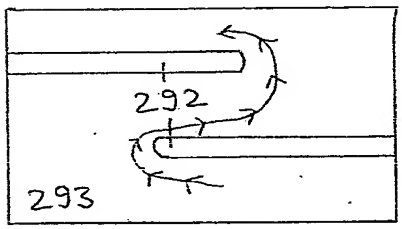

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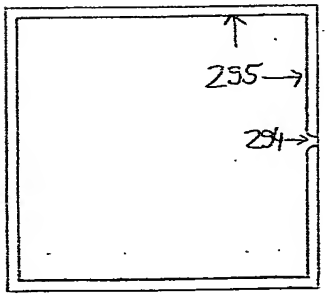

FIG. 6
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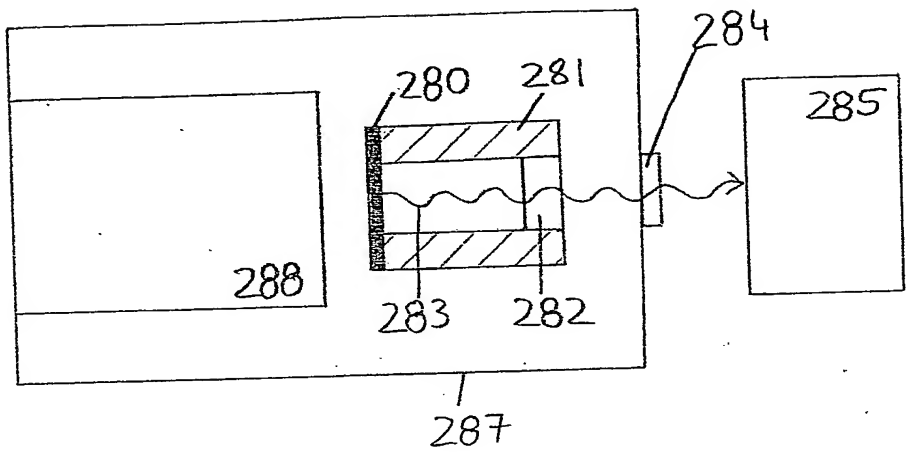

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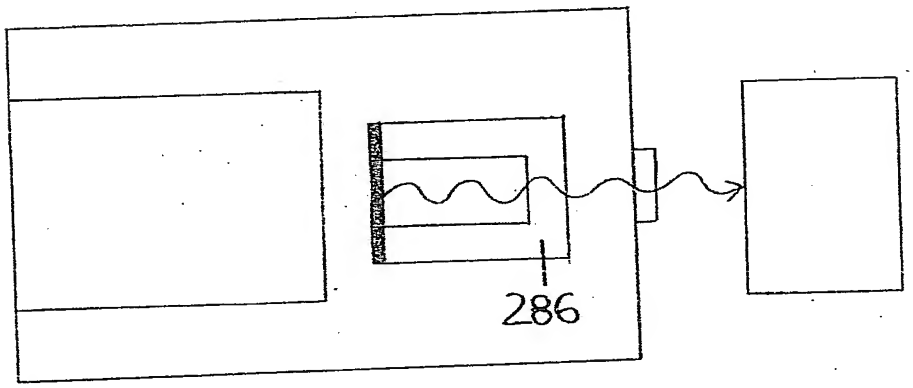

FIG. 7